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TERRESTRIAL C SEQUESTRATION AT ELEVATED CO_2 AND TEMPERATURE: THE ROLE OF DISSOLVED ORGANIC N LOSS

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Abstract. We used a simple model of carbon–nitrogen (C–N) interactions in terrestrial ecosystems to examine the responses to elevated CO_2 and to elevated CO_2 plus warming in ecosystems that had the same total nitrogen loss but that differed in the ratio of dissolved organic nitrogen (DON) to dissolved inorganic nitrogen (DIN) loss. We postulate that DIN losses can be curtailed by higher N demand in response to elevated CO_2, but that DON losses cannot. We also examined simulations in which DON losses were held constant, were proportional to the amount of soil organic matter, were proportional to the soil C:N ratio, or were proportional to the rate of decomposition. We found that the mode of N loss made little difference to the short-term (<60 years) rate of carbon sequestration by the ecosystem, but high DON losses resulted in much lower carbon sequestration in the long term than did low DON losses. In the short term, C sequestration was fueled by an internal redistribution of N from soils to vegetation and by increases in the C:N ratio of soils and vegetation. This sequestration was about three times larger with elevated CO_2 and warming than with elevated CO_2 alone. After year 60, C sequestration was fueled by a net accumulation of N in the ecosystem, and the rate of sequestration was about the same with elevated CO_2 and warming as with elevated CO_2 alone. With high DON losses, the ecosystem either sequestered C slowly after year 60 (when DON losses were constant or proportional to soil organic matter) or lost C (when DON losses were proportional to the soil C:N ratio or to decomposition). We conclude that changes in long-term C sequestration depend not only on the magnitude of N losses, but also on the form of those losses.

Key words: carbon–nitrogen interactions; carbon sequestration; dissolved inorganic nitrogen; dissolved organic nitrogen; ecosystem models; global climate change; soil C:N; terrestrial ecosystems.

INTRODUCTION

Terrestrial ecosystems are thought to sequester ~25% of the carbon (C) currently emitted through fossil-fuel burning and land use change (IPCC 2001). It is hoped that these ecosystems will continue to be a major sink for C in the future and thereby mitigate further increases in CO_2 in the atmosphere. However, productivity in terrestrial ecosystems is strongly constrained by the dynamics of the nitrogen (N) cycle (Vitousek et al. 1998) and C sequestration is likely to require a net accumulation of N in these ecosystems. The input of N to ecosystems has been widely studied, especially from the perspective of atmospheric N deposition (Ollinger et al. 1993, Galloway et al. 2003, 1995) and an understanding of the controls on biological N_2 fixation is emerging (Cleveland et al. 1999, Rastetter et al. 2001, Vitousek et al. 2002). However, surprisingly little is known about the form, magnitude, or controls of N losses from terrestrial ecosystems (Sollins and McCorrison 1981, Hedin et al. 1995, Aber et al. 2002, McDowell 2003, Neff et al. 2003; Pellerin et al., 2004). In this paper we argue that the amount of C sequestered in terrestrial ecosystems in response to elevated CO_2 depends on the fraction of N losses that are in the form of dissolved organic N (DON) vs. dissolved inorganic N (DIN). Because plants can curtail DIN losses as N demand increases in response to elevated CO_2, but plants have little control over DON losses, the potential for accumulating N by limiting N losses should be small if DON losses are high. Thus, the potential for sequestering C in response to elevated CO_2 should be small if a large fraction of the N losses are as DON.

Modifications to the Standard Model

Our assessment of C sequestration in relation to DON losses relies upon three modifications to what has been called ''the standard model'' of N accumulation in terrestrial ecosystems (Vitousek et al. 1998). First, as suggested by Vitousek et al. (1998) and Neff et al. (2003), the standard model needs to be modified to include DON losses. Second, the standard model needs to be modified to accommodate an increase in N demand by both plants and microbes in response to el-

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evated CO_2 levels. Finally, the dynamics of DIN in the standard model have to be modified to reflect the fact that N uptake by microorganisms, N uptake by plants, and N losses from the ecosystems happen simultaneously rather than sequentially. These changes will be discussed in more detail.

We have made several assumptions to simplify our analysis. The first relates to the growing evidence that plants can use organic forms of N (Chapin et al. 1993, Kieland 1994, Schimel and Chapin 1996, McKane et al. 2002, Neff et al. 2003, Schimel and Bennett 2003). We circumvent this complication by lumping plant-available forms of DON into the DIN pool and use ''DON'' to refer only to unavailable forms. By lumping plant-available forms of DON into the DIN pool, we are also assuming that these forms of DON are available to soil microbes. We further simplify our analysis by assuming that any additional DON available to microbes is retained in the ecosystems and therefore can be lumped with the soil organic N (Lipson and Monson 1998, Perakis and Hedin 2001). Thus, we assume that the DON lost from ecosystems is in a form that is unavailable to both plants and microbes. We also assume that there is no change in the ratio of NH_4 to NO_3 in soil solution so that the DIN losses can be represented as proportional to the total DIN in soil solution. Finally, we lump gaseous N losses (e.g., denitrification) in with DIN losses.

DON losses

Until recently, DON losses from terrestrial ecosystems have been largely ignored (Campbell et al. 2000, Goodale et al. 2000) and were not incorporated into the standard model of N accumulation (Vitousek et al. 1998). Estimates that infer total N losses from stream chemistry indicate that DON losses range from $<$20% to $>$80% of those losses (e.g., Goodale et al. 2000, McHale et al. 2000, Buffam et al. 2001, Perakis and Hedin 2002, Qualls et al. 2002). Because of retention and processing of DON and DIN in the vadose zone, ground water, riparian areas, and streams (Newbold et al. 1981, 1982, Hedin et al. 1998, Kroeger 2003), stream water chemistry probably does not faithfully reflect the chemistry of water leaving the rooting zone of upland areas. For example, Currie et al. (1996) found that DON accounted for $>$97% of the N in zero-tension lysimeters at the base of the rooting zone of a previously logged New England forest, whereas Goodale et al. (2000) found that, on average, DON accounted for only 67% of the N in steams draining previously logged New England forests. In a southern hardwood forest, Qualls et al. (2002) found N fluxes to be 92% DON in the B horizon, 75% in the C horizon, and 79% in the stream. In addition, none of these studies quantifies the fraction of DON that might be available to either plants or microbes. Thus, although DON losses appear to be important, the relative losses of DIN vs. DON from upland ecosystems are far from certain (McDowell 2003). Our purpose here is not to resolve this uncertainty but rather to assess the consequences of DIN vs. DON losses on the potential for C sequestration in terrestrial ecosystems in response to elevated CO_2 concentrations.

Increased N demand in response to elevated CO_2

The standard model of N accumulation is formulated from the perspective of a single limiting resource (i.e., N) and therefore does not address the effects of other resources, such as CO_2, on N dynamics. An alternate perspective is provided by the ''functional equilibrium hypothesis'' (Bloom et al. 1985, Chapin et al. 1987, Farrar and Jones 2000), which predicts that increased CO_2 concentrations will free plant resources currently allocated toward C acquisition and allow them to be reallocated toward the acquisition of other resources such as N. This hypothesis has been corroborated in several studies on tree saplings, in which allocation to fine roots increased in response to elevated CO_2 (e.g., Prior et al. 1997, Janssens et al. 1998, Tingey et al. 2000), and also has been observed in intact forest stands, although the response is weaker than in studies on saplings (Matamala and Schlesinger 2000, Pritchard et al. 2001). This compensatory reallocation of internal resources should increase N-uptake potential of plants. In addition, elevated CO_2 should increase the flux of C to soils in litter and root exudates and thereby increase microbial N demand (Mikan et al. 2000, Johnson et al. 2001). These responses of plants and microbes to elevated CO_2 should decrease soil DIN concentrations and therefore decrease DIN losses, resulting in an increase in N accumulation in the ecosystem (until enough N accumulates in the ecosystem to meet the demand through internal N recycling). However, this mechanism for accumulating N requires that N losses from the ecosystem be in a form that is available to plants and microbes; therefore this mechanism will not work if N is lost as an unavailable form of DON.

Simultaneity of DIN uptake and loss processes

In the standard model of N accumulation in terrestrial ecosystems (Vitousek et al. 1998), inorganic N entering the soil by gross mineralization or deposition is assumed to satisfy microbial needs first (immobilization), then to satisfy plant needs (plant uptake), and only then is N lost from the ecosystem. This heuristic simplification arose for two reasons. First, by assuming that microbes have first access to the available N, the model could be formulated directly on net N mineralization, which is readily estimated, and there would be no need to estimate gross mineralization, which is far more difficult (Nadelhoffer et al. 1985, Hart et al. 1994, Bosatta and Ågren 1995). Second, by assuming that N losses only occur after plant requirements are met, the model could focus on N-breakthrough dynamics associated with N saturation (Aber et al. 1998). In an ecosystem approaching N saturation, the rate of N inputs as net mineralization plus deposition is higher than plant requirements. Nitrate therefore builds up in the soil, which results in accelerated N losses through denitrification and leaching of the highly mobile nitrate ions.

These simplifications in the standard model could be problematic for analyses of ecosystem response to elevated CO_2 because they do not allow for changes in the competitive interactions between plants and microbes for available N, or for decreases in ecosystem N losses in response to increased N demand by plants and microbes. Although soil microbes clearly have a substantial competitive advantage over plants for acquiring N, that advantage is not so overwhelming as to exclude plant N uptake until microbial N demand is fully satisfied. Nor are plants so effective at acquiring N that they can completely shut off DIN losses from the ecosystem. Thus, as CO_2 increases, plant N demand and C fluxes to the soil should increase, which should result in a shift in the relative rates of plant uptake, microbial immobilization, and ecosystem losses. To account for this shift in relative rates, the three processes have to be modeled as occurring simultaneously, a perspective that has been greatly facilitated by the development of stable isotope techniques (e.g., Nadelhoffer et al. 1999, Perakis and Hedin 2001). Our purpose here is to assess how this shift in the relative rates of plant uptake, microbial immobilization, and ecosystem losses might differ if N losses are as DON vs. DIN and how that difference might affect C sequestration in response to elevated CO_2.

ANALYSIS

Our hypothesis is easily conceptualized from the perspective of an ecosystem initially at steady state. Under this steady state, N losses exactly equal N inputs to the ecosystem, so there is no net N accumulation. If an increase in CO_2 then results in higher N demand by plants and microbes, DIN losses will decline and N will accumulate in the ecosystem until enough N builds up and is recycled within the ecosystem to meet the higher N demand, at which point a new steady state is reached. However, because we assume that DON losses are in a form that is unavailable to plants and microbes, the rate of N accumulation by this mechanism cannot exceed the initial rate of DIN loss. The actual rate of N accumulation will depend upon how low the DIN concentrations can be decreased in response to increased N demand by plants and microbes. The amount of C sequestered will depend upon how the accumulated N is distributed among ecosystem components and if there is any change in the C:N ratio of those components. To assess this potential for C sequestration, we have implemented DON losses into the Multiple-Element Limitation (MEL) model (Rastetter and Shaver 1992, Rastetter et al. 1997, 2001).

Modifications to the MEL model

The MEL model was designed to examine responses of terrestrial ecosystems to changes in CO_2 and N deposition under the constraints of mass balance on both C and N and the feedbacks associated with N recycling through the soil (Tables 1 and 2). The C and N cycles are coupled through the acclimation of C and N uptake rates by vegetation to maintain the ratio of C:N in plant tissues (Eqs. 6 and 21 in Table 1) and through the adjustment of microbial N immobilization and C and N assimilation efficiencies to maintain the microbial C:N ratio (Eqs. 24–29). The C:N ratio and growth of vegetation are constrained by simple assumptions about allometry and biomass allocation to wood (Eq. 8). The DIN pool is simultaneously available to plants, to microbes, and for losses from the ecosystem (Eqs. 15, 22, and 24). The model and its parameterization for a northeastern United States mixed forest at steady state are fully documented in Rastetter et al. (2001).

For our analysis here, we added equations to simulate both dissolved organic C (DOC) and DON losses. We assume that the DON loss rate (L_{DON}, in grams of N per square meter per year) is proportional to the DOC loss rate (L_{DOC}, in grams of C per square meter per year); $L_{\mathrm{DON}} = L_{\mathrm{DOC}}/\theta_{\mathrm{DOM}}$, where θ_{DOM} is the C:N ratio of the dissolved organic matter lost from the ecosystem. We further assumed that this C:N ratio is constant, with a value of 30 g C/g N (the average for old-growth watersheds reported in Goodale et al. 2000). A more dynamic representation of the C:N ratio of dissolved organic matter must wait for better empirical assessment of how those dynamics are regulated.

To explore various controls on DOC losses, we developed four alternate models (in the following equations, β_{DOC} is a constant with units that differ for the four models (Table 3).

1) *Constant-loss model:* $L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}}$. This is the simplest possible model. In it we assume a constant DOC loss rate and therefore no feedbacks from other ecosystem properties.

2) *Proportional-loss model:* $L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}} D_{\mathrm{C}}$. In this model we assume that DOC losses are proportional to the amount of organic matter in the soil (D_{C}), as was found by Neff et al. (2000) for Hawaiian soils of varying ages. This formulation provides a feedback that increases DOC losses in response to any process that increases the accumulation of soil organic C (e.g., higher litter inputs or slower decomposition rates).

3) *C:N-based model:* $L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}}\, D_{\mathrm{C}}/D_{\mathrm{N}}$. In this model we assume that DOC losses are proportional to the soil C:N ratio ($D_{\mathrm{C}}/D_{\mathrm{N}}$), as found by Aitkenhead and McDowell (2000) for a global relationship across 15 types of biome. In this formulation, losses of DOC again increase with increasing soil organic C, but decrease with increasing soil organic N. The feedbacks therefore involve the complex interactions among the inputs of C and N in litter, decomposition, and N mineralization and immobilization.

4) R_{m}-based model: $L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}} R_{\mathrm{Cm}}$. In this model we assume that DOC losses are proportional to microbial respiration (R_{Cm}). Brooks et al. (1999) found a

TABLE 1. Model equations.

$$\frac{dE_{\mathrm{N}}}{dt} = R_{\mathrm{Ne}} + R_{\mathrm{Nm}} - L_{\mathrm{Ne}} - U_{\mathrm{Nm}} - U_{\mathrm{Nv}} \tag{1}$$

$$\frac{dB_{\mathrm{C}}}{dt} = U_{\mathrm{Cv}} - R_{\mathrm{Cv}} - L_{\mathrm{Cv}} \tag{2}$$

$$\frac{dB_{\mathrm{N}}}{dt} = U_{\mathrm{Nv}} - L_{\mathrm{Nv}} \tag{3}$$

$$\frac{dD_{\mathrm{C}}}{dt} = L_{\mathrm{Cv}} - R_{\mathrm{Cm}} - L_{\mathrm{DOC}} \tag{4}$$

$$\frac{dD_{\mathrm{N}}}{dt} = L_{\mathrm{Nv}} + U_{\mathrm{Nm}} - R_{\mathrm{Nm}} - L_{\mathrm{DON}} \tag{5}$$

$$\frac{dV_{\mathrm{C}}}{dt} = \begin{cases} -aAV_{\mathrm{C}} & \text{if } A > 0 \\ -aAV_{\mathrm{N}} & \text{if } A < 0 \end{cases} \tag{6}$$

$$\frac{dV_{\mathrm{N}}}{dt} = -\frac{dV_{\mathrm{C}}}{dt} \tag{7}$$

$$B_{\mathrm{A}} = \frac{B_{\mathrm{Amax}} c B_{\mathrm{C}}}{B_{\mathrm{Amax}} + cB_{\mathrm{C}}} \tag{8}$$

$$q = \frac{B_{\mathrm{C}} q_{\mathrm{min}} q_{\mathrm{max}}}{B_{\mathrm{A}} q_{\mathrm{max}} + (B_{\mathrm{C}} - B_{\mathrm{A}}) q_{\mathrm{min}}} \tag{9}$$

$$S_{\mathrm{C}} = b_{\mathrm{C}} V_{\mathrm{C}} B_{\mathrm{A}} \tag{10}$$

$$S_{\mathrm{N}} = b_{\mathrm{N}} V_{\mathrm{N}} B_{\mathrm{A}} \tag{11}$$

$$G_{\mathrm{C}} = \frac{g_{\mathrm{C}} C_{\mathrm{a}}}{(k_{\mathrm{C}} + C_{\mathrm{a}})} \tag{12}$$

$$G_{\mathrm{N}} = \frac{g_{\mathrm{N}} N}{(k_{\mathrm{N}} + N)} \tag{13}$$

$$U_{\mathrm{Cv}} = G_{\mathrm{C}} I_0 (1 - e^{-k_{\mathrm{I}} S_{\mathrm{C}}}) \tag{14}$$

$$U_{\mathrm{Nv}} = G_{\mathrm{N}} (1 - e^{-k_{\mathrm{S}} S_{\mathrm{N}}}) \tag{15}$$

$$r_{\mathrm{Nup}} = \frac{G_{\mathrm{C}} b_{\mathrm{C}} k_{\mathrm{I}}}{G_{\mathrm{N}} b_{\mathrm{N}} k_{\mathrm{S}}} e^{k_{\mathrm{S}} S_{\mathrm{N}} - k_{\mathrm{I}} S_{\mathrm{C}}} \tag{16}$$

$$U_{\mathrm{Nfix}} = \begin{cases} \dfrac{g_{\mathrm{Nfix}} S_{\mathrm{N}} (r_{\mathrm{Nup}} - r_{\mathrm{Nfix}})}{k_{\mathrm{Nfix}} + (r_{\mathrm{Nup}} - r_{\mathrm{Nfix}})} & \text{if } r_{\mathrm{Nup}} > r_{\mathrm{Nfix}} \\ 0 & \text{otherwise} \end{cases} \tag{17}$$

$$L_{\mathrm{Cv}} = m_{\mathrm{A}} B_{\mathrm{A}} + m_{\mathrm{W}} (B_{\mathrm{C}} - B_{\mathrm{A}}) \tag{18}$$

$$L_{\mathrm{Nv}} = \frac{qB_{\mathrm{N}}}{B_{\mathrm{C}}} \left[\frac{m_{\mathrm{A}}}{q_{\mathrm{A}}} B_{\mathrm{A}} + \frac{m_{\mathrm{W}}}{q_{\mathrm{W}}} (B_{\mathrm{C}} - B_{\mathrm{A}}) \right] \tag{19}$$

$$R_{\mathrm{Cv}} = r_{\mathrm{A}} B_{\mathrm{A}} + r_{\mathrm{W}} (B_{\mathrm{C}} - B_{\mathrm{A}}) \tag{20}$$

$$A = \ln\left(\frac{B_{\mathrm{C}}}{qB_{\mathrm{N}}} \right) + h \left(\frac{1}{B_{\mathrm{C}}} \frac{dB_{\mathrm{C}}}{dt} - \frac{1}{B_{\mathrm{N}}} \frac{dB_{\mathrm{N}}}{dt} \right) \tag{21}$$

$$L_{\mathrm{Ne}} = \beta_{\mathrm{Ne}} E_{\mathrm{N}} \tag{22}$$

$$\theta = \frac{\varepsilon_{\mathrm{N}} \phi}{\varepsilon_{\mathrm{C}}} \tag{23}$$

$$U_{\mathrm{Nm}} = \frac{\psi \alpha_{\mathrm{N}} D_{\mathrm{C}}^2 N}{\theta D_{\mathrm{N}} (\kappa_{\mathrm{Nm}} + N)} \tag{24}$$

$$M_{\mathrm{N}} = \psi D_{\mathrm{N}} + U_{\mathrm{Nm}} \tag{25}$$

$$\Lambda_{\mathrm{C}} = \frac{\varepsilon_{\mathrm{C}} \theta M_{\mathrm{N}}}{\psi D_{\mathrm{C}} + \theta M_{\mathrm{N}}} \tag{26}$$

$$\Lambda_{\mathrm{N}} = \frac{\varepsilon_{\mathrm{N}} \psi D_{\mathrm{C}}}{\psi D_{\mathrm{C}} + \theta M_{\mathrm{N}}} \tag{27}$$

$$R_{\mathrm{Cm}} = \psi D_{\mathrm{C}} (1 - \Lambda_{\mathrm{C}}) \tag{28}$$

$$R_{\mathrm{Nm}} = M_{\mathrm{N}} (1 - \Lambda_{\mathrm{N}}) \tag{29}$$

$$\left.\begin{array}{ll} \text{Constant-loss model:} & L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}} \\ \text{Proportional-loss model:} & L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}} D_{\mathrm{C}} \\ \text{C:N-based model:} & L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}} \dfrac{D_{\mathrm{C}}}{D_{\mathrm{N}}} \\ R_{\mathrm{m}}\text{-based model:} & L_{\mathrm{DOC}} = \beta_{\mathrm{DOC}} R_{\mathrm{Cm}} \end{array}\right\} \tag{30}$$

$$L_{\mathrm{DON}} = L_{\mathrm{DOC}} / \theta_{\mathrm{DOM}} \tag{31}$$

similar relationship, but for over-winter rates of soil respiration. Again DOC losses increase with higher soil organic C stocks, but also increase with elevated temperature.

We present simulations for both high (5:1) and low (1:5) ratios of DON : DIN losses. In the original parameterization with no DON losses (Rastetter et al. 2001), the steady-state DIN losses were 0.6 g $\mathrm{N \cdot m^{-2} \cdot yr^{-1}}$ to match the annual deposition rate. In the new model, the initial, steady-state DON and DIN losses were 0.5 and 0.1 g $\mathrm{N \cdot m^{-2} \cdot yr^{-1}}$ for the high-DON-loss simulations, and 0.1 and 0.5 g $\mathrm{N \cdot m^{-2} \cdot yr^{-1}}$, for the low-DON-loss simulations (Table 3). With a constant dissolved organic matter C:N ratio of 30 g C/g N, the DOC losses were 15 and 3 g $\mathrm{C \cdot m^{-2} \cdot yr^{-1}}$ in the high- and low-DON-loss simulations, respectively. To incorporate these additional C and N losses and maintain the assumption of an initial steady state, we had to compensate by adjusting parameters regulating the rates of other fluxes in the model (Table 3). To compensate for the additional loss of C from the soil organic matter as DOC, we decreased microbial respiration by decreasing ψ (Table 1, Eq. 28), which also decreased gross N mineralization (Table 1, Eqs. 25 and 29), but not enough to fully compensate for the loss of N as DON. To fully compensate for the DON losses, we increased N immobilization by increasing α_{N} (Table 1, Eq. 24). Relative to the original parameterization, the changes in ψ and α_{N} were ~3% for the high-DON-loss simulations and ~1% for the low-DON-loss simulations. All other fluxes and all the initial C and N stocks are as reported in Rastetter et al. (2001).

Simulations

We ran four simulations with each of the four DON-loss models. In these simulations, we examined the responses with both high and low DON losses to an instantaneous doubling of CO_2 concentration or to an

TABLE 2. Model variables and parameters.

Term	Definition	Units
A	acclimation potential	
a	acclimation rate	yr^{-1}
B_A	active-tissue C in plants	$g\ C/m^2$
B_{Amax}	maximum B_A	$g\ C/m^2$
B_C	C in plant biomass	$g\ C/m^2$
b_C	leaf area per unit C	$m^2/g\ C$
B_N	N in plant biomass	$g\ N/m^2$
b_N	root length per unit C	m/g C
c	allometric parameter	
C_a	CO_2 concentration	mL/m^3
D_C	C in soil detritus	$g\ C/m^2$
D_N	N in soil detritus	$g\ N/m^2$
g_C	canopy-level quantum yield	g C/MJ
G_C	substrate-corrected g_C	$g\ C \cdot m^{-2} \cdot yr^{-1}$
g_N	maximum plant N uptake	$g\ N \cdot m^{-2} \cdot yr^{-1}$
G_N	substrate-corrected g_N	$g\ N \cdot m^{-2} \cdot yr^{-1}$
g_{Nfix}	N fixation constant	$g^2\ N \cdot g^{-1}\ C \cdot m^{-2} \cdot yr^{-1}$
h	acclimation damping	yr
I_0	above-canopy irradiance	$MJ \cdot m^{-2} \cdot yr^{-1}$
k_C	half-saturation for CO_2	mL/m^3
k_I	light extinction	m^2/m^2
k_N	plant half-saturation for N	$g\ N/m^2$
k_{Nfix}	half-saturation fixation cost	g C/g N
k_S	soil-resource extinction	m^2/m
L_{CD}	organic-C leaching	$g\ C \cdot m^{-2} \cdot yr^{-1}$
L_{Cv}	litter C loss	$g\ C \cdot m^{-2} \cdot yr^{-1}$
L_{DOC}	DOC loss	$g\ C \cdot m^{-2} \cdot yr^{-1}$
L_{DON}	DON loss	$g\ N \cdot m^{-2} \cdot yr^{-1}$
L_{Ne}	inorganic-N leaching	$g\ N \cdot m^{-2} \cdot yr^{-1}$
L_{Nv}	litter N loss	$g\ N \cdot m^{-2} \cdot yr^{-1}$
m_A	active-tissue-litter loss rate	yr^{-1}
m_W	woody-tissue-litter loss rate	yr^{-1}
N	inorganic N	$g\ N/m^2$
q	plant optimal C:N	g C/g N
q_A	active-tissues-litter C:N	g C/g N
q_{max}	maximum plant C:N	g C/g N
q_{min}	minimum plant C:N	g C/g N
q_W	woody-tissue-litter C:N	g C/g N
r_A	active-tissue respiration rate	yr^{-1}
R_{Cm}	microbial respiration	$g\ C \cdot m^{-2} \cdot yr^{-1}$
R_{Cv}	plant respiration	$g\ C \cdot m^{-2} \cdot yr^{-1}$
R_{Ne}	external N supply	$g\ N \cdot m^{-2} \cdot yr^{-1}$
R_{Nm}	N mineralization	$g\ N \cdot m^{-2} \cdot yr^{-1}$
r_{Nfix}	cost of N fixation	g C/g N
r_{Nup}	cost of N uptake	g C/g N
r_W	woody-tissue respiration rate	yr^{-1}
S_C	leaf area	m^2/m^2
S_N	root length	m/m^2
t	time	yr
U_{Cv}	gross photosynthesis	$g\ C \cdot m^{-2} \cdot yr^{-1}$
U_{Nm}	microbial N uptake	$g\ N \cdot m^{-2} \cdot yr^{-1}$
U_{Nv}	plant N uptake	$g\ N \cdot m^{-2} \cdot yr^{-1}$
V_C	plant C-uptake effort	
V_N	plant N-uptake effort	
α_N	microbial N-uptake	g N/g C
β_{Ne}	inorganic-N loss rate	yr^{-1}
β_{DOC}	DOC loss rate	varies, see Table 3
ε_C	maximum microbial C efficiency	
ε_N	maximum microbial N efficiency	
θ	C:N microbial consumption	g C/g N
θ_{DOM}	C:N dissolved organic matter	g C/g N
κ_{Nm}	microbial N half-saturation	$g\ N/m^2$
Λ_C	microbial C efficiency	
Λ_N	microbial N efficiency	
M_N	microbial N consumption	$g\ N \cdot m^{-2} \cdot yr^{-1}$
ϕ	C:N microbial byproducts	g C/g N
ψ	decomposition rate	yr^{-1}

TABLE 3. Initial steady-state fluxes and associated parameter values for processes altered in this application of the MEL model.

Flux	Associated parameter	Original value	High DON-loss value	Low DON-loss value	Units
DOC loss (L_{DOC})		0	15	3	$g\ C \cdot m^{-2} \cdot yr^{-1}$
	β_{DOC} (M1)		15	3	$g\ C \cdot m^{-2} \cdot yr^{-1}$
	β_{DOC} (M2)		0.00115	0.000231	yr^{-1}
	β_{DOC} (M3)		0.601	0.120	$g\ N \cdot m^{-2} \cdot yr^{-1}$
	β_{DOC} (M4)		0.0277	0.00542	g C/g C
DON loss (L_{DON})		0	0.5	0.1	$g\ N \cdot m^{-2} \cdot yr^{-1}$
	θ_{DON}		30	30	g N/g C
DIN loss (L_{Ne})		0.6	0.1	0.5	$g\ N \cdot m^{-2} \cdot yr^{-1}$
	β_{Ne}	0.231	0.0385	0.192	yr^{-1}
Microbial respiration (R_{Cm})		556	541	553	$g\ C \cdot m^{-2} \cdot yr^{-1}$
	ψ	0.0508	0.0495	0.0505	yr^{-1}
Gross N mineralization (R_{Nm})		60.75	60.42	60.70	$g\ N \cdot m^{-2} \cdot yr^{-1}$
N immobilization (U_{Nm})		47.25	47.42	47.30	$g\ N \cdot m^{-2} \cdot yr^{-1}$
	α_N	0.0126	0.0130	0.0127	g N/g C

Notes: Original value is the value reported in Rastetter et al. (2001). A separate value is given for β_{DOC} for each of the four equations used to simulate DOC loss (M1, constant-loss model; M2, proportional-loss model; M3, C:N-based model; M4, R_m-based model).

instantaneous doubling of CO_2 concentration and a 4°C increase in temperature, which is the predicted temperature change for New England over the next 100 years (IPCC 2001). All simulations began at a steady state and were allowed to run to a new steady state following the change in CO_2 or CO_2 and temperature. By imposing an instantaneous change in CO_2 or CO_2 and temperature, responses that act at different time scales tend to be segregated as the simulation proceeds; responses associated with fast mechanisms appear first and those associated with slower mechanisms emerge later. To assess the effects of a more realistic scenario, we ran 100-year simulations with CO_2 or CO_2 and temperature (+4°C) increasing linearly over the 100 years. This gradual change tends to superimpose the fast responses onto those acting on the decade-to-century time scale.

Partitioning the change in ecosystem C

To help analyze the results of our simulations, we partitioned the predicted change in total ecosystem C among four factors relating to the interactions between C and N (Rastetter et al. 1992): (1) the change in the total amount of N in the ecosystem ($\Delta C_{\Delta N_T}$), (2) the change in plant C:N ratio ($\Delta C_{\Delta C:N_P}$), (3) the change in soil C:N ratio ($\Delta C_{\Delta C:N_S}$), and (4) the redistribution of N between plants and soil ($\Delta C_{B_N \Leftrightarrow D_N}$). Rastetter et al. (1992) quantified these four factors plus their synergistic interaction ($\Delta C_{\mathrm{inter}}$):

$$\Delta C_{\Delta N_T} = (\Delta B_N + \Delta D_N)\frac{B_C + D_C}{B_N + D_N}$$

$$\Delta C_{\Delta C:N_P} = B_N \Delta\left(\frac{B_C}{B_N}\right)$$

$$\Delta C_{\Delta C:N_S} = D_N \Delta\left(\frac{D_C}{D_N}\right)$$

$$\Delta C_{B_N \Leftrightarrow D_N} = \left(\frac{B_C}{B_N} - \frac{D_C}{D_N}\right)\left[\frac{(\Delta B_N)D_N - (\Delta D_N)B_N}{B_N + D_N}\right]$$

$$\Delta C_{\mathrm{inter}} = \Delta B_N \Delta\left(\frac{B_C}{B_N}\right) + \Delta D_N \Delta\left(\frac{D_C}{D_N}\right)$$

where B_C and B_N are the C and N initially in plant biomass, D_C and D_N are the C and N initially in soil detritus (litter plus soil organic matter), ΔB_N and ΔD_N are the changes in the plant and soil N, and $\Delta(B_C/B_N)$ and $\Delta(D_C/D_N)$ are the changes in the plant and soil C:N ratio. The changes in C associated with these factors are comprehensive and mutually exclusive; thus the total change in ecosystem C is the sum of the changes associated with each factors plus their interaction.

To implement these equations, we simply ran the MEL model to predict values for plant and soil C and N stocks (i.e., B_C, B_N, D_C, and D_N), calculated the changes in the N stocks and C:N ratios from their initial values, and plugged these values into the equations. In this way, the cumulative effect of each factor can be assessed at any time during the simulations.

RESULTS AND DISCUSSION

Terrestrial ecosystems display a wide range of DON vs. DIN losses across ecological and biophysical gradients and in response to anthropogenic factors. Our simulations indicate that these N loss variations can have important consequences for ecosystem carbon accumulation under changing CO_2 and temperature regimes. After 1000 years of simulated exposure to doubled CO_2 alone and to doubled CO_2 with 4°C warming, we found that ecosystems with high DON losses accumulated 1.5–4 times less carbon than ecosystems with low DON losses (Table 3). Steady-state differences in carbon accumulation were even greater, with the greatest effect being observed under elevated CO_2 and temperature (Fig. 1).

The divergent patterns of C accumulation observed in our simulations arise from differences in the accumulation and internal cycling of N, and involve several mechanisms acting at different time scales. In our earlier analysis of responses to elevated CO_2, but without DON losses (Rastetter et al. 1997), we identified four distinct mechanisms acting on different time scales: (1) the nearly instantaneous response of the photosynthetic enzyme system, (2) the 1–10 year, within-plant acclimation to reestablish a balance in the C vs. N uptake rates, (3) the 50–80 year redistribution of N between soils and plants, and (4) the long-term accumulation of N. For the analysis presented here, the first three of these mechanisms can be lumped into a single category of within-ecosystem mechanisms. Our results indicate that these within-ecosystem mechanisms dominate the dynamics during the first 60 years of the simulations, and that the slow accumulation of N by the ecosystem dominates the dynamics thereafter.

Responses during the first 60 years

During the first 60 years of the simulations with doubled CO_2 concentration alone, the behaviors of the models are almost identical; there is very little difference in the amount or rate of C sequestration between simulations with high vs. low DON losses or among the four DON-loss models (Fig. 1). During this period, differences in N accumulation are too small to have a noticeable effect on C sequestration relative to the within-ecosystem mechanisms for C sequestration. The major mechanism of C sequestration during this early response is a redistribution of N from soils to vegetation (Fig. 2, Table 4). When the CO_2 concentration is increased, plants compete more effectively against soil microbes for available N, so there is a net loss of N from soils and a concurrent net N gain by plants (Fig. 1). Because the C:N ratio of soils is ~25 and that of plants is ~143 (initial C:N values), this redistribution of N results in a net increase in the amount of

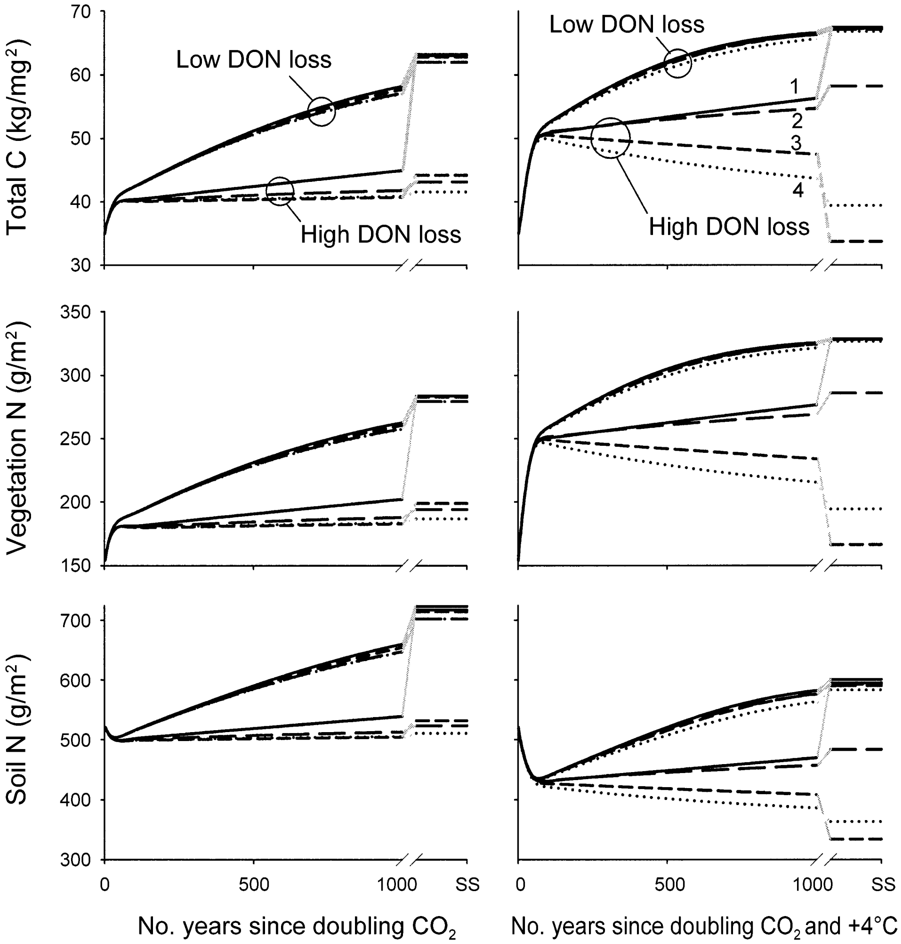

FIG. 1. Responses of the MEL model to an instantaneous doubling in CO$_2$ concentration (left column) or an instantaneous doubling in CO$_2$ concentration plus 4°C warming (right column). Results are for simulations with low or high DON (dissolved organic nitrogen) losses (as indicated in the upper panels). Line types indicate the results from four DON-loss models (as indicated in upper right panel) that differ in how DOC and DON losses are controlled: (1) constant-loss model, (2) proportional-loss model, (3) C:N-based model, and (4) R_m-based (microbial respiration) model. The results at year 1000 for vegetation and soil N follow the same sequence from top to bottom as the results for total C in the upper panels. The final steady state (SS) is indicated on the right of each panel following the break in the *x*-axis.

C stored per unit N in the ecosystem. Although there is a net loss of N from the soil during these first 60 years, soil C actually increases because of higher plant productivity and litterfall. The soil C:N ratio therefore increases and also contributes to the amount of C stored per unit N in the ecosystem (Fig. 2). Elevated CO$_2$ increased plant production and biomass, which, in a mature, closed-canopy forest, results in a larger increase in woody tissues, with a high C:N ratio, than in leaves and fine roots (i.e., active tissues), with a much lower C:N ratio. Thus, increases in the plant C:N ratio also contributed slightly to an increase the C stored per unit N in the ecosystem.

When the ecosystem is warmed in addition to increasing CO$_2$, the results are again nearly identical during the first 60 years between simulations with high vs. low DON losses and among the four DON-loss models (Fig. 1). However, N redistribution from soils to plants is enhanced because of direct stimulation of N mineralization by warming (Fig. 3). Thus the amount of N redistributed and the resulting C accumulation are larger under both elevated CO$_2$ and higher temperatures than under elevated CO$_2$ alone. Warming also stimulates microbial respiration, resulting in a short-lived ($<$10 years) decrease in soil C that is quickly compensated for by higher litter inputs. Within about 30 years, these litter inputs increase the soil C:N ratio above its initial value, which contributes to an increase in the C stored per unit N in the ecosystem. The combined effects of elevated CO$_2$ and of warming-induced increases in N availability stimulate plant production and biomass more than elevated CO$_2$ alone. Thus, with a combination of elevated CO$_2$ and warming, increases in woody tissues and the consequent increase in plant C:N ratio contribute significantly to an increase the C stored per unit N in the ecosystem (Fig. 2). By year

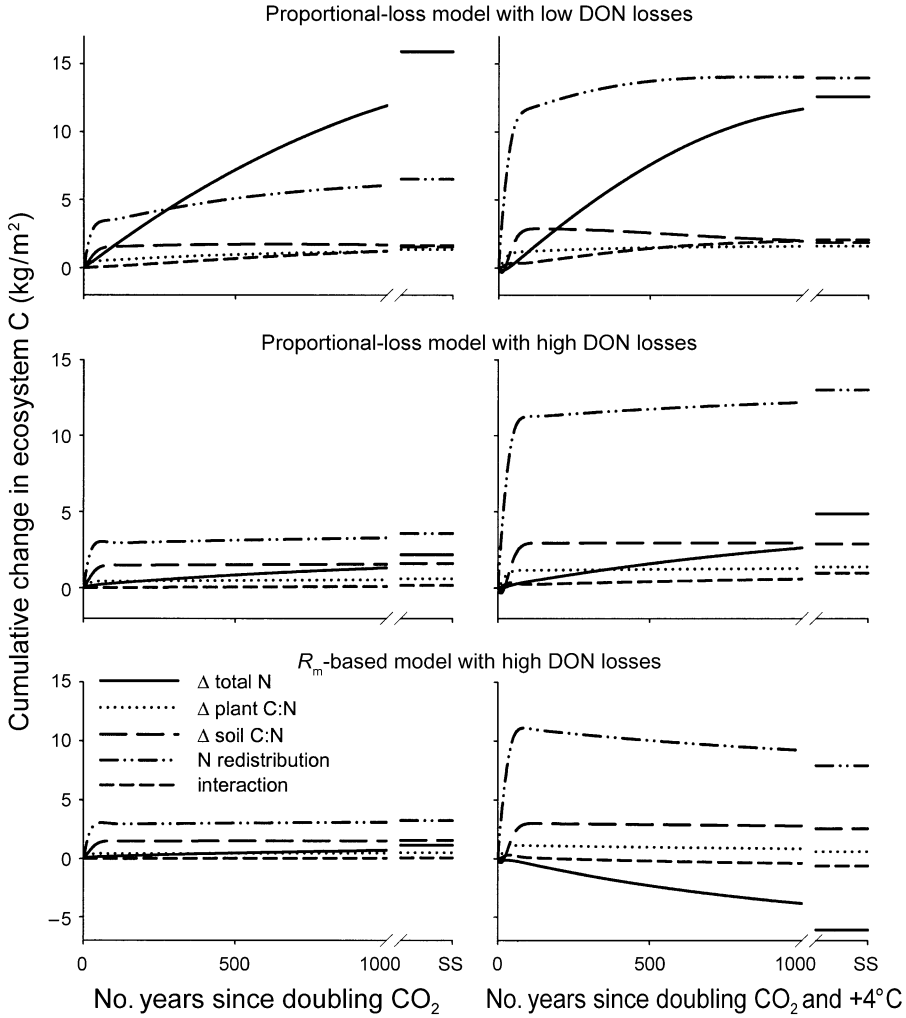

FIG. 2. Partitioning of the cumulative change in ecosystem C following a doubling of CO_2 concentration (left column) or following a doubling of CO_2 concentration and 4°C warming (right column) among four factors. Shown are the cumulative changes in C associated with total changes in ecosystem N (Δ total N), with changes in plant C:N ratios (Δ plant C:N), with changes in soil C:N ratios (Δ plant C:N), with the redistribution of N between plants and soils (N redistribution), or with the interaction among these four factors (interaction) for the proportional-loss model with low and high DON losses and for the R_{m}-based model with high DON losses. The changes in ecosystem C associated with these factors and their interaction sum to the total change in ecosystem C shown in Fig. 1 for the respective models. The final steady state (SS) is indicated on the right of each panel following the break in the *x*-axis.

60, the simulations with both elevated CO_2 and warming sequester ~2.5 times as much C as with only elevated CO_2.

Responses after year 60 with low DON losses

With low DON losses, the amount of C stored after year 60 does not differ much among the four DON-loss models in either the simulations with elevated CO_2 alone or with elevated CO_2 and warming. This concordance among models results from the low cumulative losses of DON relative to the other N fluxes in the models. The differences among DON-loss models therefore are not strongly manifested in the rates of N accumulation. Sequestration of C continues for the duration of all low-DON-loss simulations, although at a rate that is only ~17% of that during the first 60 years (Fig. 1, Table 4). Most of the C accumulation after year 60 is associated with the net accumulation of N by the ecosystem (Fig. 2, Table 4).

For the low-DON-loss simulations, the amount of C accumulated between years 60 and 1000 is about the same with elevated CO_2 alone as it is with elevated CO_2 and warming (~16 kg C/m^2; Fig. 1, Table 4). In both sets of simulations, increases in plant and microbial N demand draw down DIN concentrations. However, there is a diminishing return of increases in N demand on DIN concentration as the DIN concentrations decline. Thus, although N demand differs between the two sets of simulations, DIN concentrations decrease to about the same level and place similar limits on plant productivity. Loss

TABLE 4. Simulated changes in ecosystem C at 60 and 1000 years after an instantaneous doubling of CO_2 concentration or an instantaneous doubling of CO_2 concentration and a 4°C increase in temperature.

	Dissolved organic nitrogen (DON) loss									
	Average of all models at year 60		Constant-loss model at year 1000		Proportional-loss model at year 1000		C:N-based model at year 1000		R_m-based model at year 1000	
DON-loss model	Low	High	Low	High	Low	High	Low	High	Low	High
Doubling of CO_2 only										
$\Delta C_{\Delta N_T}$	0.97	0.21	12.85	3.43	11.95	1.33	12.44	0.62	11.88	0.72
$\Delta C_{\Delta C:N_P}$	0.52	0.45	1.24	0.71	1.21	0.54	1.23	0.47	1.21	0.48
$\Delta C_{\Delta C:N_S}$	1.42	1.42	1.65	1.65	1.68	1.56	1.66	1.52	1.69	1.53
$\Delta C_{B_N \Leftrightarrow D_N}$	3.40	3.05	6.15	3.89	6.06	3.29	6.10	3.07	6.05	3.10
$\Delta C_{\mathrm{inter}}$	0.07	0.02	1.32	0.28	1.23	0.09	1.28	0.04	1.22	0.05
$\Delta C_{\mathrm{total}}$	6.39	5.15	23.21	9.96	22.13	6.81	22.71	5.72	22.05	5.88
Doubling of CO_2 and +4°C										
$\Delta C_{\Delta N_T}$	0.45	0.08	12.06	3.70	11.69	2.65	11.73	−1.71	10.89	−3.81
$\Delta C_{\Delta C:N_P}$	1.16	1.15	1.59	1.34	1.59	1.29	1.59	1.03	1.57	0.86
$\Delta C_{\Delta C:N_S}$	2.22	2.31	1.95	2.92	2.02	2.96	2.01	2.93	2.16	2.81
$\Delta C_{B_N \Leftrightarrow D_N}$	10.86	10.71	13.98	12.55	14.03	12.20	14.01	10.30	14.09	9.22
$\Delta C_{\mathrm{inter}}$	0.34	0.28	2.00	0.78	1.97	0.60	1.97	−0.10	1.89	−0.39
$\Delta C_{\mathrm{total}}$	15.02	14.53	31.58	21.29	31.30	19.70	31.31	12.45	30.60	8.69

Notes: The simulations are for four DON-loss models that differ in the way DON losses are controlled and for both low and high initial DON-loss rates. The total change in ecosystem C ($\Delta C_{\mathrm{total}}$) has been partitioned among factors associated with (1) changes in total ecosystem N ($\Delta C_{\Delta N_T}$), (2) changes in plant C:N ratios ($\Delta C_{\Delta C:N_P}$), (3) changes in soil C:N ratios ($\Delta C_{\Delta C:N_S}$), (4) a redistribution of N between plants and soils ($\Delta C_{B_N \Leftrightarrow D_N}$), and (5) the interactions of the changes in total N, C:N ratios, and N redistribution ($\Delta C_{\mathrm{inter}}$).

rates of DIN are therefore about the same and the net rates of N accumulation are comparable. Because N accumulation in the ecosystem is the major mechanism of C sequestration after year 60 (~70% of total; Fig. 2), the rates of C accumulation are also about the same in the elevated CO_2 alone and in the elevated CO_2 and temperature simulations. However, in response to elevated CO_2 alone, the low-DON-loss ecosystems accumulate an additional ~5 kg C/m^2 after year 1000 before eventually approaching a steady state (~2500 years); in response to both elevated CO_2 and temperature, the ecosystems sequester <1 kg C/m^2 after year 1000.

Changes in plant and soil C:N ratios contribute substantially less to C sequestration than does N accumulation after year 60 in the low-DON-loss simulations (Fig. 2, Table 4). Plant C:N ratios increase because of an increase in wood relative to leaves and roots, but the associated contribution to C sequestration is <5% of the total change between years 60 and 1000. The C:N ratio of soils remains almost constant in the elevated CO_2 simulations and actually declines back toward its initial value in the elevated CO_2 plus warming simulations. Thus changes in the soil C:N ratio contribute little or negatively (−1.1% to 1.5% of the total) to C sequestration after year 60 (Fig. 2).

After year 60 in these low-DON-loss simulations, the rate of N accumulation in plants per unit N already in plants is only slightly higher than the rate of N accumulation in soils per unit N already in soil (Fig. 1). In our four-factor analysis, this slight difference in the relative rates of N accumulation is reflected in the small increase in C accumulation attributable to N redistribution after year 60 (15–20% of the total; Fig. 2). This nearly equal relative rate of N accumulation in plants and soils indicates that the competitive balance between plants and microbes has been almost reestablished after year 60.

The synergistic interaction among the four factors in our analysis also contributes to C sequestration after year 60 of the low-DON-loss simulations (7–10% of the total; Fig. 2). This interactive effect results mostly from the net accumulation of N in ecosystem components with C:N ratios that had increased during the first 60 years of the simulation. Thus, new N accumulating in the ecosystem has an enhanced effect on C sequestration because of the higher C:N ratios.

Responses after year 60 with high DON losses

Averaged over all four DON-loss models, the ecosystems with high DON losses sequestered ~1.9 kg C/m^2 between years 60 and 1000 under elevated CO_2 alone (Fig. 1). This C accumulation amounted to ~38% of the C sequestered in the first 60 years and only ~12% of the C sequestered between years 60 and 1000 by the ecosystems with low DON losses. Before reaching a steady state, the high-DON-loss ecosystems accumulated, on average, an additional ~6 kg C/m^2, but this average increase was due almost entirely to C accumulation in the constant-loss model (Fig. 1; see discussion that follows). The major mechanism for C sequestration was again N accumulation in the ecosystem (Table 4). However, because most of the N losses were as unavailable DON, N accumulated at only 12% of the rate in the ecosystems with low DON losses. The within-ecosystem mechanisms of C sequestration (changes in plant and soil C:N ratio and N redistribution between plants and soils) cumulatively contrib-

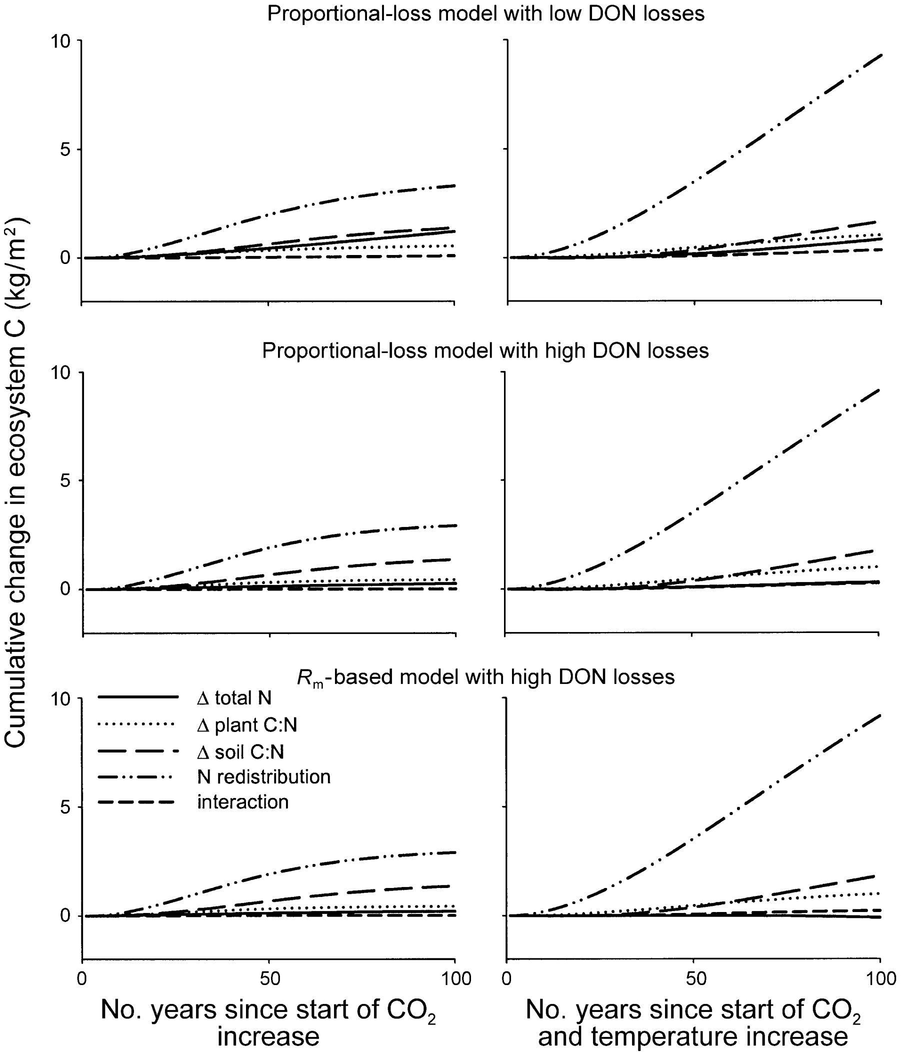

FIG. 3. Partitioning of the cumulative change in ecosystem C during a gradual doubling of CO_2 concentration over 100 years (left column) or during a gradual doubling of CO_2 concentration and 4°C warming over 100 years (right column) among four factors. Shown are the cumulative changes in C associated with total changes in ecosystem N (Δ total N), with changes in plant C:N ratios (Δ plant C:N), with changes in soil C:N ratios (Δ plant C:N), with the redistribution of N between plants and soils (N redistribution), or with the interaction among these four factors (interaction) for the proportional-loss model with low and high DON losses and for the R_m-based model with high DON losses.

uted only 30% of the C storage between years 60 and 1000, compared to 96% of the C storage during the first 60 years. All of the mechanisms of C sequestration differed substantially among the DON-loss models (Fig. 2) and will be discussed further.

Under elevated CO_2 and temperature and high DON losses, the four DON-loss models diverged substantially (Figs. 1 and 2). On average, the ecosystems sequestered only ~1 kg C/m^2 between years 60 and 1000 or ~7% of the C sequestered during the first 60 years and ~6% of the C sequestered in the ecosystems with low DON losses (Fig. 1). After year 1000, the models continued to diverge, with changes in C storage ranging from an additional gain of ~18 kg C/m^2 to a loss of ~14 kg C/m^2 before reaching a steady state (Fig. 1; see discussion that follows). These ecosystems only accumulated N at 1% of the rate of the ecosystems with low DON losses and at 10% of the rate at which they accumulated N under elevated CO_2 alone (Table 4). The major mechanisms of C sequestration were an increase in soil C:N ratio (59% of the total) and a redistribution of N from soils to plants (36% of the total). The mechanisms of C sequestration again differed among DON-loss models (Fig. 2) and are will be discussed further.

Because of the explicit linkages between DOC and DON in the various model structures, simulations with higher DON loss also exhibit higher DOC loss. Thus, the ecosystems with high DON losses lost 12–15 kg·m^{-2}·1000 yr^{-1} more C as DOC than did the ecosystems with low DON losses. These differences are about the same magnitude as the differences in total C sequestration between the two sets of simulations. However, the differences in DOC loss do not account for differences in C sequestration under elevated CO_2 or elevated CO_2 and temperature. Indeed, these differences in DOC loss were present at the initial steady state, prior to imposed changes in CO_2 or temperature. In addition, higher DOC losses in the high-DON-loss simulations were exactly compensated for by lower microbial respiration (see the section on *Modifications to the MEL model*). To test the importance of direct C losses as DOC, we reran all of the simulations with a DOC : DON ratio of 15 rather than 30. Thus, relative to the original simulations, there was the same DON loss but only half of the DOC loss. After 1000 years, there was a $<1.2\%$ difference in the resulting C and N stocks for the R_m-based model, and $<0.3\%$ difference for the other three models. In contrast, the differences in N retention between the low- and high-DON-loss simulations resulted in differences in NPP of 87–159 kg $C \cdot m^{-2} \cdot 1000\ yr^{-1}$ or ~10 times the net difference in C sequestration. Clearly the direct C losses as DOC exert only a marginal influence on ecosystem C sequestration relative to the effects of DON losses.

Comparison of individual DON-loss models

Patterns of ecosystem N and C accumulation were virtually identical for the four DON-loss models in the initial 60 years, the period when internal N redistribution dominated ecosystem dynamics. However, DON-loss model behaviors diverged sharply between years 60 and 1000, particularly with high DON losses and the combination of elevated CO_2 plus warming.

By year 1000, the constant-loss model accumulated substantially less C in response to elevated CO_2 alone in the high-DON-loss simulations than in the low-DON-loss simulations (~5 vs. 17 kg C/m^2). However, at steady state, C sequestration was similar in high- vs. low-DON-loss simulations because of similar N accumulation. Similar steady-state N pools develop because both simulations have the same constant rate of DON loss, and total N losses (DON plus DIN) must equal the total (constant) N inputs to the ecosystem. As a result, N eventually accumulates in both simulations until the DIN losses equal the initial DIN losses. This condition is met when soil DIN concentrations build up to their initial values, which were identical for the two simulations. Thus, both the low- and high-DON-loss simulations converge on the same soil fertility at steady state, which in turn results in virtually identical steady-state values for vegetation biomass and soil organic matter (Fig. 2). However, it takes about five times as long to accumulate enough N and approach that steady state with high DON losses than with low DON losses.

In response to elevated CO_2 alone, the other three models accumulate $<10\%$ the C between years 60 and 1000 with high DON losses as with low DON losses (<1.7 vs. >15 kg C/m^2; Fig. 1). The steady-state C and N stocks in these other three models are also much lower with high DON losses than with low DON losses, and are only slightly higher than the stocks after 1000 years. As with the constant-loss model, these models also have to accumulate enough N for the DON plus DIN losses to equal N inputs at steady state. However, unlike the constant-loss model, DON losses in these other models increase as soil C increases (proportional-loss model), as the soil C:N ratio increases (C:N-based model), or as soil respiration increases (R_m-based model). Because all three of these ecosystem characteristics increase in the simulations, the models accumulate nitrogen 2.5–6 times more slowly than the constant-loss model (Table 4). The higher rates of DON loss, and consequently slower rates of N accumulation in the other three models, are indirectly associated with the increase in productivity during the first 60 years. Higher productivity increases litterfall and soil C, which increase DON losses in the proportional-loss model. The higher soil C stocks and a net decline in soil N (Fig. 2) increase soil C:N ratios, which increase DON losses in the C:N-based model. The higher soil C stocks and lower C assimilation efficiency associated with higher soil C:N ratios increase the absolute rate of microbial respiration, which increases DON losses in the R_m-based model.

The accumulation of N also can have secondary effects on the within-ecosystem mechanisms for C sequestration. Because the competition between plants and microbes for N shifts toward plants when CO_2 increases, the relative rate of N accumulation increases more in plants than in soils, especially before year 60. In the constant-loss model with high DON losses, this redistribution of N persists after year 60, but at a much slower rate. Because there was no appreciable net accumulation of ecosystem N in any of the other models between years 60 and 1000, and because the competitive balance between plants and microbes had become reestablished, the redistribution of N did not contribute to C sequestration after year 60 in these simulations. The C:N ratios of both plants and soils remained almost constant after year 60 in all four models and therefore also did not contribute to C sequestration.

With both elevated CO_2 and warming, the four models diverged substantially after year 60 in the high-DON-loss simulations (Figs. 1 and 2, Table 4). The constant-loss and proportional-loss models sequestered C in the ecosystem and gained N in both plants and soils, but at about one-fourth of the rate in the low-DON-loss simulations (Fig. 1). The C:N-based and R_m-based models lost C from the ecosystem and N from the plants and soils. The primary mechanism for these patterns is a net accumulation of ecosystem N after year 60 in the constant-loss and proportional-loss models, and a net N loss after year 60 in the C:N-based and R_m-based models (Fig. 2). Secondarily, in the simulations that gained N (constant-loss and proportional-

TABLE 5. Simulated changes in ecosystem C after 100 years with CO_2 concentration doubling linearly over the 100 years or with CO_2 concentration doubling and temperature increasing by 4°C over the 100 years.

	DON loss							
	Constant-loss		Proportional-loss		C:N-based		R_m-based	
Model	Low	High	Low	High	Low	High	Low	High
Doubling of CO_2 only								
$\Delta C_{\Delta N_T}$	1.24	0.34	1.23	0.27	1.22	0.20	1.22	0.22
$\Delta C_{\Delta C:N_P}$	0.55	0.45	0.55	0.45	0.55	0.44	0.55	0.44
$\Delta C_{\Delta C:N_S}$	1.38	1.38	1.38	1.38	1.38	1.38	1.38	1.38
$\Delta C_{B_N \Leftrightarrow D_N}$	3.33	2.93	3.33	2.93	3.33	2.92	3.33	2.92
ΔC_{inter}	0.09	0.02	0.09	0.02	0.09	0.02	0.09	0.02
ΔC_{total}	6.59	5.12	6.58	5.05	6.57	4.97	6.57	4.98
Doubling of CO_2 and +4°C								
$\Delta C_{\Delta N_T}$	0.83	0.26	0.84	0.31	0.81	0.15	0.76	−0.10
$\Delta C_{\Delta C:N_P}$	1.04	1.01	1.04	1.01	1.03	1.01	1.03	1.00
$\Delta C_{\Delta C:N_S}$	1.67	1.80	1.67	1.79	1.68	1.81	1.69	1.85
$\Delta C_{B_N \Leftrightarrow D_N}$	9.38	9.23	9.38	9.23	9.39	9.24	9.40	9.26
ΔC_{inter}	0.34	0.26	0.34	0.27	0.34	0.25	0.34	0.22
ΔC_{total}	13.27	12.56	13.28	12.61	13.25	12.46	13.21	12.23

Notes: The simulations are for four DON-loss models that differ in the way DON losses are controlled and for both low and high initial DON-loss rates. The total chance in ecosystem C (ΔC_{total}) has been partitioned among factors associated with (1) changes in total ecosystem N ($\Delta C_{\Delta N_T}$), (2) changes in plant C:N ratios ($\Delta C_{\Delta C:N_P}$), (3) changes in soil C:N ratios ($\Delta C_{\Delta C:N_S}$), (4) a redistribution of N between plants and soils ($\Delta C_{B_N \Leftrightarrow D_N}$), and (5) the interactions of the changes in total N, C:N ratios, and N redistribution (ΔC_{inter}).

loss models), the persistent competitive advantage of plants favored N redistribution from soils to plants, which increased C sequestration (Fig. 2). In the simulations that lost N (C:N-based and R_m-based models), the relative redistribution of N was from plants to soils because the net loss of N limits production and the decline in plant biomass precedes the decline in soil organic matter. Thus, although the redistribution of N during the first 60 years resulted in a net accumulation of C, the loss of N eventually overwhelmed the dynamics, causing the ecosystem to rebound and lose C. The C:N ratios of both plants and soils again remained almost constant after year 60 in all four models.

These differences among models in the high-DON-loss simulations arise because of differences in the sensitivities of the DON-loss mechanisms to warming. In the constant-loss model, DON losses are constant and therefore not sensitive to warming. Thus, after year 60, N continues to accumulate in the constant-loss model with both elevated CO_2 and warming for the same reasons and at about the same rate as with elevated CO_2 alone (Table 4). In the proportional-loss model, DON losses are proportional to soil C stocks, which initially decline because of higher respiration when the ecosystem is first warmed, but then recover as litter inputs increase. The DON losses eventually increase as soil C stocks build, but by only about two-thirds as much as in the simulation with elevated CO_2 alone. Therefore, N accumulation is higher in the proportional-loss model with elevated CO_2 and warming than with elevated CO_2 alone. In the C:N-based model, DON loss is proportional to the soil C:N ratio, which increases during the first 60 years of the simulation because of increased litter inputs and a net loss of N to the plants. The higher net N mineralization and higher litter inputs with warming result in even higher soil C:N ratios with elevated CO_2 plus warming than with elevated CO_2 alone. Therefore, the C:N-based model loses N faster with elevated CO_2 plus warming than with elevated CO_2 alone and there is a net loss of N from the ecosystem. In the R_m-based model, DON losses are proportional to microbial respiration, which increases with warming and with higher soil C stocks. Therefore, the R_m-based model loses N faster with elevated CO_2 plus warming than with elevated CO_2 alone and there is a net loss of N from the ecosystem.

Responses to gradual increases in CO_2 or CO_2 plus warming

In the simulations with a gradual doubling of CO_2 or gradual doubling of CO_2 plus a 4°C warming over 100 years, the relatively fast responses associated with within-ecosystem mechanisms (primarily N redistribution) were superimposed on the slower responses associated with N accumulation by the ecosystem. Thus the responses that dominated during the first 60 years under an instantaneous increase in CO_2 or CO_2 plus temperature were spread out over the 100-year simulations and had not fully developed by the end of the simulations (Fig. 3, Table 5). However, the instantaneous and gradual-change simulations eventually reached identical steady states.

As in the first 60 years of the instantaneous-change simulations, the redistribution of N from soils to vegetation dominated the response during the 100 years of the gradual-change simulations and the effect of this mechanism on C sequestration was higher with elevated CO_2 plus warming than with elevated CO_2 alone

(Fig. 3, Table 5). Increases in plant and soil C:N ratios contributed less to C sequestration, but in amounts proportionately equivalent to their contributions in the instantaneous-change simulations. With low DON losses, ecosystem N accumulated during the first 100 years in the gradual-change simulations at ~68–75% of the rate observed in the instantaneous-change simulations, primarily because N demands track the gradual increase in CO_2. With high DON losses, N gains and losses were small during the first 100 years of all the simulations, and the dynamics in the gradual-change simulations generally lagged behind those in the instantaneous-change simulations by about two decades.

CONCLUSIONS

The major conclusion from our analysis is that DON losses can have significant effects on the long-term sequestration of C in terrestrial ecosystems in response to elevated CO_2 and warming. Because our simulations consider forms of DON that are not available to plants or microbes (e.g., Neff et al. 2003), DON losses cannot be attenuated when elevated CO_2 concentrations increase ecosystem N demand, whereas DIN losses can. Thus, high rates of DON loss relative to DIN loss result in lower rates of ecosystem net N accumulation, and hence lower C sequestration, in response to elevated CO_2. This mechanism for constraining C sequestration is similar to the mechanism proposed by Hedin et al. (1995) and Vitousek et al. (1998) for the persistence of N limitation late into succession.

What general characteristics of the C and N cycles promote C sequestration in our simulations? Potential C sequestration is greatest when the ratio of DON:DIN is small, when there is a high N throughput by the ecosystem, when there is a large and prolonged depletion of DIN in response to elevated N demand, and when there is a large amount of C stored per unit N in the ecosystem (i.e., a high ecosystem C:N ratio). The first three characteristics determine the rate of N accumulation in response to elevated CO_2, and the last determines the C return associated with that N accumulation. Each of these characteristics varies widely among ecosystems (e.g., DIN vs. DON, Goodale et al. 2000, Perakis and Hedin 2002; rates of N throughput, Likens et al. 1977, Aber et al. 1998; DIN depletion in response to elevated N demand, Hungate et al. 1997, Finzi and Schlesinger 2003; and variable ecosystem C:N ratios, Vitousek et al. 1988) and has potential to affect C sequestration. Although our simulations primarily highlight the important, yet overlooked, role of variations in DON vs. DIN losses on C sequestration, we expect that many other factors, including disturbance regimes and nutrient limitation patterns, are also likely to be important. For example, in simulations of clear cutting, high DIN losses promoted even greater N losses during the first 10–15 years of recovery as plant N uptake reestablished (data not shown). However, after ~60 years of recovery under elevated CO_2, N demand lowers DIN concentration and the high-DIN-loss ecosystems retain more N than the high-DON-loss ecosystems, thus increasing C sequestration (for a more thorough assessment of N losses and disturbance, see Hungate et al. 2003). Our analysis can also be extended to consider losses of dissolved organic forms of phosphorus, which may be particularly important in P-limited tropical ecosystems (Hedin et al. 2003) or in temperate regions where accelerated N deposition has relaxed N limitation.

Despite the potentially large consequences of DON losses on N accumulation and C sequestration, our analysis indicates that these effects are slow to emerge and may take millennia to develop fully. Within-ecosystem mechanisms, such as N redistribution and changes in plant and soil C:N ratios (e.g., Hooker and Compton 2003), dominated short-term C sequestration in response to elevated CO_2 and temperature. The long-term impact of ecosystem N accumulation on C sequestration will remain difficult to evaluate empirically, independent of effects from shorter term mechanisms, yet such dynamics can be captured through ecosystem simulation models. Moreover, because these mechanisms operate at different time scales, short-term observations cannot be used to assess long-term responses (Rastetter 1996).

The degree to which the long-term effects of DON losses are masked by faster within-ecosystem responses depends on their relative strength at any particular time. From our analysis, within-ecosystem responses are rapid and are dominated by the redistribution of N from soils to vegetation. The magnitude of this effect is proportional to the difference between the C:N ratios of vegetation and soil. This difference is large if the vegetation is woody, suggesting that the effects of DON losses will be more strongly masked, and for a longer duration, in woody ecosystems. In addition, increases in plant and soil C:N ratios can contribute to the within-ecosystem responses and help to mask the effects of DON losses. The effects of DON losses would therefore be more effectively masked by within-ecosystem N cycling processes in ecosystems that become more woody in response to elevated CO_2 and warming (e.g., Sturm et al. 2001).

Our analysis also indicates that the way in which DON losses are regulated can affect long-term C sequestration, provided that DON losses are large relative to DIN losses. Although ecological factors such as N inputs, disturbance, climate, and succession are thought to influence broad patterns of N loss (Sollins and McCorison 1980, Hedin et al. 1995, Goodale et al. 2000, Perakis and Hedin 2002), we lack information on the mechanisms that regulate relative DIN vs. DON losses from ecosystems. Variation in the availability and remineralization of different DON forms to DIN (Qualls and Haines 1992), as well as direct incorporation of DIN into DON (Dail et al. 2001, Perakis and Hedin 2001), provide further complexity that was not captured by our simulations. Our simulations indicate that different mechanisms of DON regulation can yield responses similar to some perturbations but not others (e.g., the similarity among models in the responses to elevated CO_2 vs. their divergence in response to elevated CO_2 plus temperature). Yet despite such uncertainty, results from our four DON-loss models consistently indicate that as DON losses increase in response to the changing environment (e.g., warming), the effects of high DON losses will be exacerbated (i.e., C sequestration decreased).

Losses of DON are accompanied by a direct loss of C as DOC. We assumed a constant C:N ratio for these two losses, but compensated for the difference in C loss between low- vs. high-DON-loss simulations by adjusting microbial respiration. Our analysis indicates that the direct losses of C as DOC do not play a major role in terrestrial C sequestration. Thus, differences in the C:N ratio of dissolved organic matter leaching out of the ecosystems should have only a minor influence on C sequestration. Far more important is the direct loss of N as DON and its consequent effects on fertility and plant production. The differences in productivity between our low- and high-DON-loss simulations were an order of magnitude greater than the differences in the cumulative losses of C as DOC. Nevertheless, even small changes in DOC leaching may signal large changes in terrestrial C storage (e.g., Freeman et al. 2001).

On a regional or global scale, the fate of DON lost from the ecosystem also has ramifications for C sequestration. The initial C:N ratio of our simulated ecosystem (plants plus soils) is 52. Therefore if the DON is later transformed and entrained into the N cycle of an ecosystem with a higher C:N ratio (e.g., a system with a larger woody component), then it would contribute to C sequestration. On the other hand, if it is buried as is (C:N ~30) or gets entrained into an ecosystem with a lower C:N ratio (e.g., a planktonic ecosystem), then the loss of that DON would decrease C sequestration.

Because of the very long time constants associated with the effects of DON losses on the responses of terrestrial ecosystems to elevated CO_2 plus warming, the results of our analysis will be very difficult to test (Rastetter 1996). Furthermore, it will be difficult to find pairs of ecosystems that differ in their relative rates of DON vs. DIN loss, but do not differ in some other fundamental way that affects responses to elevated CO_2 plus warming. The best potential for testing our ideas in a timely manner would be to experimentally manipulate ecosystems where the masking effects of within-ecosystem responses are likely to be small relative to the effects of DON losses, to determine if there is a trend toward high C sequestration with low DON losses relative to DIN losses. Thus the manipulations should be on ecosystems where the C:N ratio of vegetation is low (i.e., close to the C:N ratio of soils so that the redistribution of N has a smaller effect), where the vegetation is unlikely to increase in woodiness (i.e., to avoid the masking effects of increasing C:N ratios), and where the total throughput of DON plus DIN is high (i.e., a high potential to sequester N). Marshes might be ideal candidates if they are demonstrably N limited.

Our aim in this paper has been to examine how a consideration of the relative magnitudes of DON vs. DIN losses might influence assessments of potential C sequestration in terrestrial ecosystems. Our conclusions are that it is vital to quantify these fluxes, at least in regard to evaluations of the long-term potential for C sequestration. Because the mechanism underlying the DON–DIN effect is the attenuation of DIN losses by plants and microbes, it is important to quantify these fluxes as they leave the rooting zone before transformation along hydrologic flow paths through deep soils, groundwaters, and riparian zones to surface waters. Furthermore, it is important to distinguish between DON that is available to plants and microbes and DON that is not. Clearly DON in soils comprises a wide range of compounds with a continuum of availabilities to both plants and microbes, and our analysis examines responses at the extremes of this continuum. Although our basic conclusions would not be altered with a more realistic representation of DON availability, we recognize that predictive assessments of the long-term potential for C sequestration in response to elevated CO_2 plus climate change requires improved understanding and quantification of losses of DIN and all forms of DON.

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